

NASA TECHNICAL NOTE

NASA TN D-3148

NASA TN D-3148

DISSEMINATION INFORMATION  
Approved for public release  
Distribution Unlimited

19960628 049

# AN EXPLORATORY STUDY OF A NEW CLASS OF STEPLADDER AND LADDER POLYMERS - POLYIMIDAZOPYRROLONES

by George F. Pezdirtz and Vernon L. Bell

Langley Research Center

Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1965

DEPARTMENT OF DEFENSE  
ASTICS STANDARDS EVALUATION CENTER  
PICATINNY ARSENAL, NEW JERSEY

DTIC QUALITY INSPECTED

NASA TN D-3148

AN EXPLORATORY STUDY OF A NEW CLASS OF STEPLADDER  
AND LADDER POLYMERS - POLYIMIDAZOPYRROLONES

By George F. Pezdirtz and Vernon L. Bell

Langley Research Center  
Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

---

For sale by the Clearinghouse for Federal Scientific and Technical Information  
Springfield, Virginia 22151 - Price \$1.00

AN EXPLORATORY STUDY OF A NEW CLASS OF STEPLADDER  
AND LADDER POLYMERS - POLYIMIDAZOPYRROLONES

By George F. Pezdirtz and Vernon L. Bell  
Langley Research Center

SUMMARY

[A new class of aromatic-heterocyclic polymers has been discovered. These were prepared from the room-temperature reaction of tetraamines with tetraacids or their respective derivatives. This new class of polymers is polyimidazopyrrolones or "Pyrroles." Exploratory experiments indicate that they have excellent thermal and radiolytic stability and hold considerable potential for aerospace as well as highly specialized terrestrial applications. The chemical structure of the Pyrroles combines the structures of the aromatic polyimides and polybenzimidazoles. Since they are formed through an intermediate stage which is soluble, typical solution property measurements can be used for basic molecular characterization. Knowledge of the molecular properties of the soluble intermediate reflect on the molecular character of the final insoluble Pyrroles. A reaction scheme for the conversion of the soluble intermediate is presented. Applied properties such as ease of fabrication, mechanical strength, and molding characteristics are discussed.]

INTRODUCTION

Many current and advanced aerospace programs have well established needs for polymeric materials which retain their useful properties at elevated temperatures of 350 to 650° C (623 to 923° K) and after exposure to high doses of radiation (1 000 to 20 000 megarads). There are also similar industrial requirements for polymers with these properties. Commercially available polymers such as those based on the phenolics, epoxies, melamines, fluoro carbons, and silicones are limited to continuous use only at temperatures up to 250° C (523° K), with intermittent use up to 350° C (623° K). There has been an intensive effort to develop new polymers with improved thermal and radiolytic stability.

Since 1955 several new classes of aromatic main chain polymers have been discovered as a result of this effort. A few of the outstanding polymers, some of which are discussed in references 1 to 13 and listed in table I, have reached commercial production in the last few years. Their current production is very limited and largely oriented toward highly specialized markets, such as wire enamels, insulation, moldings, laminates, and adhesives, for use in high-temperature service.

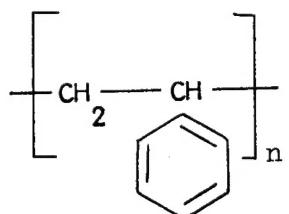
TABLE I  
SOME RECENT AROMATIC-HETEROCYCLIC POLYMERS

Aromatic-heterocyclic polymers	Thermal stability				Year	Investigators	Reference			
	Air		Inert							
	°C	°K	°C	°K						
Polyimides	400	673	500	773	1955 1963	Edwards & Robinson Bower & Frost	1(a) and 1(b) 1(c)			
Polybenzimidazoles	450	723	600	873	1961	Vogel & Marvel	2			
Polybenzothiazoles	600	873	-----	-----	1962 1964	Brumfield Hergenrother et al.	3 4			
Polybenzoxazoles	500	773	550-650	823-923	1964	Kubota & Nakanishi	5			
Polyquinoxalines	450	723	600	873	1964 1964	Stille & Williamson deGaudemaris & Sillion	6 7			
Polyparaphenylenes	500	773	-----	-----	1959 1963	Marvel & Hartzell Kovacic & Kyriakis	8 9			
Polytriazoles	---	---	500	773	1962	Lilyquist & Holdsten	10			
Polypyrazoles	---	---	450	723	1963 1965	Korshak et al. Schaefer & Bertram	11(a) 11(b)			
Polyoxadiazoles	450	723	450	723	1961 1962	Abshire & Marvel Frazer	12 13			

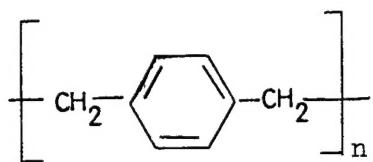
The purpose of this paper is to report on the discovery of the polyimidazo-pyrrolones, a new class of aromatic-heterocyclic polymers, and to discuss some exploratory experiments which indicate that they have unusual chemical and physical properties. The scope of these experiments is definitely exploratory and no attempt was made to optimize specific processes or properties. Indications of fruitful areas for future work will be apparent after a review of the results of these early experiments.

#### Molecular Structure

Aromatic-heterocyclic rings are most effective in protecting macromolecules from thermally and radiolytically induced rupture when they are part of the main chain itself rather than pendant to it (refs. 14 to 18). The significance of the location of the aromatic rings relative to the main chain can be seen by comparing the melting points and thermal stability of two isomeric polymers, such as polystyrene and poly-para-xylylene, which have the same ratio of aromatic rings to methylene groups (one ring to two methylenes) and differ only in the location of the ring. In isotactic polystyrene, which melts ( $T_m$ ) at  $240^\circ C$  ( $513^\circ K$ ), the aromatic ring is pendant to the chain (ref. 19). In poly-para-xylylene the ring is in the chain and the polymer melts above  $400^\circ C$  ( $673^\circ K$ ) (ref. 20).



Poly(styrene)



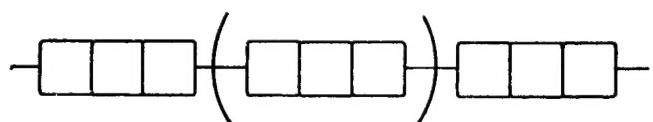
Poly(p-xyllylene)

Several stages of condensation of ring structures are possible in polymers. In the simplest case, the rings can be bonded through single links to other atoms of the chain or they can be bonded through multiple links (fused) to other rings of the chains. These structures are shown in figure 1 for general schematic models and for specific polymers. In polyphenylene the rings are attached along the chain through single links. Poly(anthracene) is an example of a "stepladder" polymer, since there are small ladder segments joined by single links. In the polyacenes the rings have a higher degree of condensation and are attached along the chain through multiple links. This case has been referred to as a ladder polymer. The most complex situation is when all rings are bound together. This material is graphite.

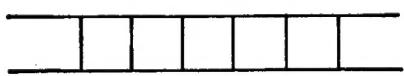
#### MODEL STRUCTURES



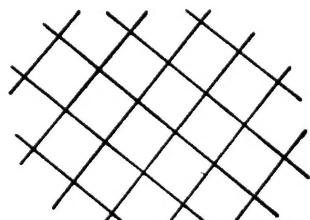
Simple linear polymer



Stepladder polymer

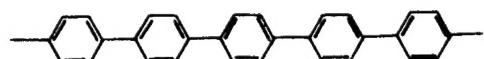


Ladder polymer

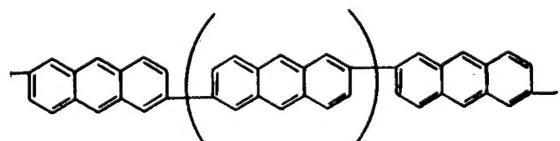


Sheet polymer

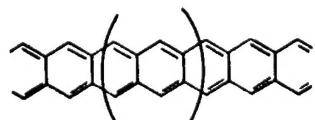
#### POLYMER STRUCTURES



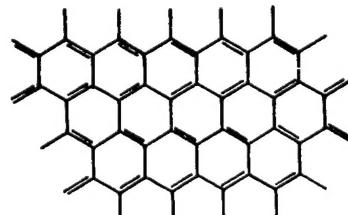
Polyphenylene



Polyanthracene



Polyacene



Graphite model

Figure 1.- Aromatic main chain structures.

The thermal, physical, and electrical properties of the various forms of graphite have been quite useful in many past and current aerospace programs. One major problem associated with the graphitic materials is the need to develop means of synthesizing these materials (or materials with comparable properties) so that they may be easily fabricated as well as "tailored" to produce specific properties for particular applications. Synthetic attempts to produce high-temperature polymers frequently have resulted in intractable "red brick dusts."

Another material with a thermal stability comparable to that of graphite is asbestos mineral (ref. 21). A prime reason for the high thermal stability of asbestos mineral can be attributed to its "ribbon-like" (ladder) molecular structure and its ability to crosslink or undergo a process wherein no chain bond is broken without being replaced by a nearby weak dative crosslink or else being directly restored. However, such ribbon polymers often lack plasticity. The polyacenes, illustrated in figure 1, might be considered to be the ribbon-type analog polymer for graphite. The polyacenes have not been made as yet with high molecular weights.

Ribbon, or double-strand, polymers have frequently been referred to as ladder polymers. In recent years a number of new classes of polymeric materials have been developed which have ladder segments along the main chain but are not considered to be complete ladder polymers. They have been referred to at various times as imperfect ladder polymers, semi-ladder polymers, block ladders, or ladder segments. These terms have been used to describe aromatic-heterocyclic main chain polymers which are imperfect ladder polymers containing some single bonds along the backbone of the chain. We prefer to classify these polymers as stepladder polymers, indicating molecular structure consisting of short ladder segments separated by single bonds as shown in figure 1. Recent theoretical studies have compared single-chain polymers undergoing degradation with the random thermal degradation of stepladder and ladder polymers (ref. 22). This analysis indicates, as one might anticipate, that the introduction of single bonds along the chain of a ladder polymer (that is, a stepladder polymer) would result in a sharp decrease in the molecular weight as degradation occurs when compared with a perfect ladder polymer. However, it should be noted that the stability of the stepladder polymer would still be much greater than that of the analogous single-chain polymer.

#### Stepladder and Ladder Polymers

The interest and research in stepladder polymers during the past few years has markedly increased; however, the work in the field of ladder polymers has proceeded at a somewhat lower rate than that of the stepladder polymers.

J. F. Brown and associates (refs. 23 and 24) have been recognized as the first to synthesize and characterize a stero-regular ladder polymer based on phenyl-trichlorosilane. There have been a few other reports (refs. 18, 25, 26, and 27) on attempts to produce ladder-type polymers, though in general the approach has been essentially the same, namely, one of addition cyclization of unsaturated pendant groups along the chain. There have been few reports (refs. 28 to 31) on cyclizations which are based on condensation reactions which could lead to ladder as well as stepladder polymers.

The literature of aromatic-heterocyclic dye chemistry provides a wealth of basic information and guidance in attempts to develop new classes of thermally and radiolytically stable ladder and stepladder polymers. The deep color and unusual thermal stability of many of these compounds have been associated with extensive conjugation of the unsaturated electron orbitals. This electronic feature is generally accepted as providing considerable delocalization of absorbed energy without subsequent permanent bond rupture. Based on this principle, one might attempt to combine the desirable molecular features of the thermally stable aromatic polyimides (PI) with the comparably stable aromatic polybenzimidazoles (PBI) in a single molecular structure as in figure 2.

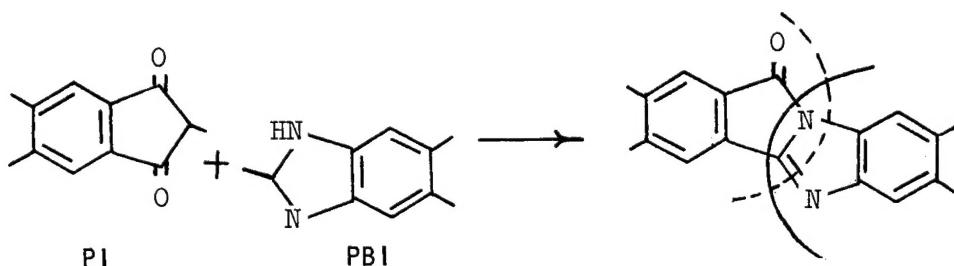


Figure 2.- Imide-imidazole fused structure.

When these structures are fused, more complex aromatic-heterocyclic classes of polymers would result which could have both stepladder and ladder molecular structures, as shown in figure 3. In the case of the stepladder structures, the fused ring system would be longer than those normally found in the PBI and PI types of polymers. In effect, the fraction of single bonds would be less than in PBI and PI polymers, and potentially this reduction of "weak links" should provide materials with enhanced thermal and radiolytic stability.

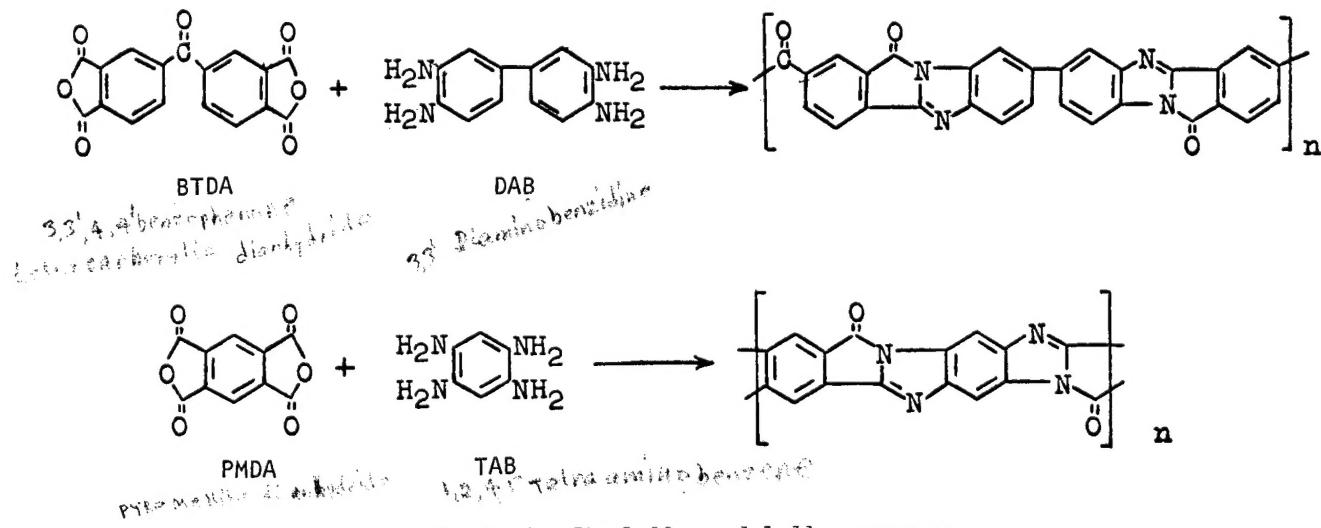


Figure 3.- Stepladder and ladder pyrrones.

## SYNTHESIS

Since aromatic polyimides and aromatic polybenzimidazoles have comparable thermal stability, which may be largely attributed to the aromatic-tetrafunctional moieties, one might consider reacting tetrafunctional monomers directly with each other. Previous work (refs. 32 and 33) describes the controlled reaction of orthodiamines with derivatives of diacids (for example, anhydrides). In the "classical" sense this reaction has been reported to give deep-red dyestuffs with high melting temperatures. Extending the functionality of this reaction by using aromatic tetraamines (or their derivatives) with aromatic tetraacids (or their derivatives) in very polar solvents has led to a new class of aromatic-heterocyclic ladder and stepladder polymers, the polyimidazopyrrolones.

### Monomer Purification

The aromatic dianhydrides could be purified by recrystallization from acetic anhydride, or by sublimation. However, recrystallization was not altogether satisfactory, since complete removal of acetic anhydride necessitated a sublimation step. It was found that a single sublimation of commercial-grade dianhydrides (pyromellitic dianhydride (PMDA) from Princeton Chemical Research and Hexagon Laboratories and 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) from Gulf Chemical Corp.) gave product equivalent in purity to material which had been recrystallized and sublimed.

Sublimation was performed at pressures of 0.5 mm Hg or less in large-capacity sublimators supplied by Kontes Glass Company. The crude dianhydride (up to 50 grams) was placed in the bottom of the vessel and covered with a circle of coarse fiber-glass fabric (to prevent mechanical carry-over of a non-sublimable powder which formed as a by-product). The inner section of the sublimator was cooled with water, whereas the heating medium was a bath of Wood's metal on a hot plate. PMDA was sublimed at temperatures of 200 to 250° C (473 to 523° K). At 200° C (473° K), 50 grams of PMDA were sublimed from 4 to 6 hours; whereas, at 250° C (523° K), the time was shortened to range from 1 to 2 hours, but at the expense of some yellow color to the product. BTDA was sublimed only at temperatures of 230 to 250° C (503 to 523° K), and the rate was somewhat slower than for PMDA.

When all the material had been sublimed, the vacuum was released and the product was scraped from the cooled surfaces of the inner condenser with a razor blade. The product was immediately stored under anhydrous conditions. The melting point of PMDA obtained with a differential scanning calorimeter was 287° C (560° K), and that of BTDA was 226° C (499° K).

3,3'-Diaminobenzidine (DAB) was obtained from Koppers Chemical Company and was purified by recrystallization from water with charcoal treatment. 1,2,4,5-Tetraaminobenzene tetrahydrochloride (TAB) (Burdick and Jackson Laboratories, Inc.) was purified by dissolving in the minimum amount of water, treating with charcoal, and reprecipitating with concentrated hydrochloric acid.

$3,3',4,4'$ -Tetraaminodiphenyl ether (TADPO) and  $3,3',4,4'$ -tetraaminodiphenyl-methane (TADPM) were prepared by catalytic hydrogenation in ethyl acetate, by using 5-percent platinum-on-charcoal catalyst at 4 atmospheres and ambient temperature.

#### Solution Polymerization (Polycondensations)

In principle, virtually any dianhydride can be reacted with orthotetraamines or their respective derivatives when both reactants are dissolved in highly polar solvents such as dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), polyphosphoric acid, and dimethyl acetamide (DMAc). Some typical dianhydrides and aromatic tetraamines which were used are listed in table II.

TABLE II

#### DIANHYDRIDES AND TETRAAMINES

Dianhydrides	Tetraamines
Pyromellitic Dianhydride (PMDA)	$1,2,4,5$ -Tetraaminobenzene (TAB)
$3,3',4,4'$ -Benzophenone Tetracarboxylic Acid Dianhydride (BTDA)	$3,3',4,4'$ -Tetraaminodiphenyl Ether (TADPO)
$1,4,5,8$ -Naphthalene Tetracarboxylic Acid Dianhydride (NTDA)	$3,3',4,4'$ -Tetraaminobiphenyl (DAB)
$1,2,3,4$ -Butane Tetracarboxylic Acid Dianhydride (BTDA)	$3,3',4,4'$ -Tetraaminodiphenyl Methane (TADPM)
$1,2,3,4$ -Cyclopentane Tetracarboxylic Acid Dianhydride (CPDA)	

When tetrafunctional compounds are used to prepare polyimidazopyrrolones, overall stoichiometry is very important if a soluble, high-molecular-weight polymer is to result. Care must be exercised in the concentrations of the reactants, the order of their combination, and the temperature at which the reaction is carried out.

#### Stepladder Polymers

As a typical example, a solution polymerization was carried out by the rapid addition of 0.0192 mole of pyromellitic dianhydride (PMDA), 4.20 grams dissolved in 40 milliliters of DMF, to a stirred solution of 0.0200 mole of

*3,3',4,4'*-tetraaminodiphenyl ether (TADPO), 4.60 grams dissolved in 35 milliliters of DMF, in a Waring Blender. The solution thickened slightly and became warm (35 to 40° C (308 to 313° K)) within 15 to 20 seconds. Stirring was continued for 5 to 10 minutes, and the solution was allowed to cool to room temperature. The remaining PMDA needed for proper stoichiometry to complete the reaction was then added dropwise from a solution of 0.30 gram (0.0014 mole) of PMDA in 5 milliliters of DMF to the stirred polymer solution until the desired viscosity level was obtained. The resulting thick polymer "dope" was centrifuged to remove bubbles and extraneous matter, such as lint and gel. The predominant product of the initial reaction consists largely of a linear, soluble polymer as shown by structure II in figure 4. When heated, this soluble polymer

undergoes two consecutive dehydration-cyclization steps by either or both of the two routes indicated in figure 4, that is, through the polybenzimidazole (IIIa) and/or polyimide (IIIb) to the final polyimidazopyrrolone (IV). The rather complicated structure for such a system can be easily drawn on paper, whereas the exact identification of all the features of such a highly complicated reaction is quite another matter. Evidence for the proposed mechanism will be discussed subsequently. Since isomers are possible from the ring opening reaction, one possible name of the final condensed polymer IV, with the indicated repeat unit (ref. 34), is poly (oxy-7H, 15H-2, 10-bisbenzimidazo [1,2-a; 1',2'-a'] benzo [1,2-c: 4,5-c']-dipyrrol-7, 15-dione). For the sake of simplicity, we have referred to this class of materials as Pyrroles.

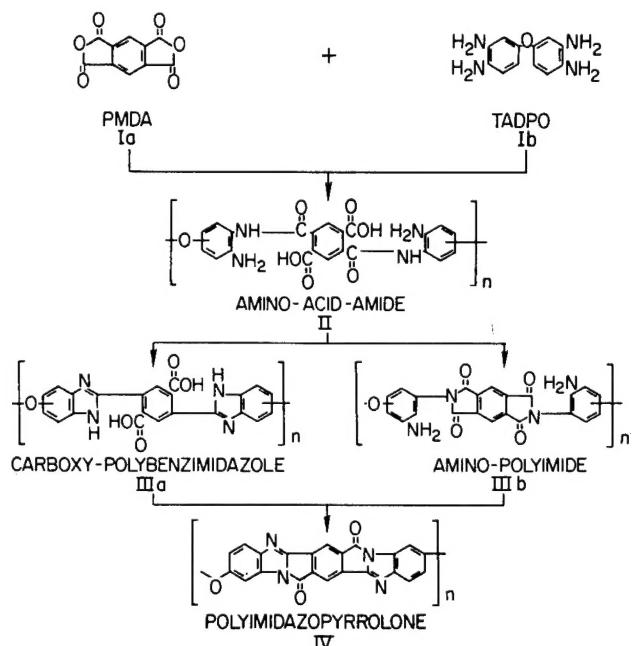


Figure 4.- Proposed reaction mechanism.

### Ladder Polymers

A similar reaction scheme was also used to prepare ladder polymers by reacting 1,2,4,5-tetraaminobenzene (TAB) with PMDA. Since both starting compounds contain fused ring(s) uninterrupted by single links the final polymer has the potential for a complete ladder structure. The TAB was used as the tetrahydrochloride salt in order to overcome the difficulties of working with the free amine which is very susceptible to oxidation.

## PHYSICAL AND CHEMICAL PROPERTIES

### Preliminary Mechanism

The reaction scheme in figure 4 represents the predominant reactions which could occur when tetraamines and dianhydrides are reacted under the conditions cited.

The infrared spectra in figure 5(a) show the changes in structure from the uncured amino-acid-amide form (A-A-A polymer) to an advanced stage of condensation. The spectra were taken from the same self-supporting 0.15-mil-thick ( $3.81 \times 10^{-4}$  cm) Pyrrone film and appear to support the overall reaction sequence shown in figure 4. The disappearance of the secondary amide bands (1650, 1540, and  $1280\text{ cm}^{-1}$ ) and the carboxyl groups at 1720, 1605, and  $1225\text{ cm}^{-1}$ , together with the appearance of an imidazole absorption at  $1620\text{ cm}^{-1}$ , and the development of the imide bands at 1765 and  $720\text{ cm}^{-1}$  are quite indicative of the proposed structure. The loss of the characteristic groups such as the amino function (3355 and  $3450\text{ cm}^{-1}$ ) and the amide-nitrogen-hydrogen stretching bands ( $3230\text{ cm}^{-1}$ ) as shown in figure 5(b) further substantiate the mechanism proposed in figure 4.

### Films

Films were easily cast by using the solutions of the A-A-A polymer which were "doctored" onto glass plates and dried at room temperature or in a forced air oven at  $125^\circ\text{ C}$  ( $398^\circ\text{ K}$ ) for 1 hour. The A-A-A film was then stripped from the glass plate and characterized or further cured to a higher degree of condensation. The A-A-A polymer, which is generally light amber in color depending upon the particular molecular structure, is quite flexible as a self-supporting film in thicknesses ranging from 0.1 to 5 mils.

Further condensation of the A-A-A film toward the Pyrrone-type structure was accomplished by continued heating for 1 hour at  $225^\circ\text{ C}$  ( $498^\circ\text{ K}$ ). During this time the film developed a deep-blood-red color indicative of a highly conjugated electronic structure and somewhat reminiscent of the classical deep-red dyes as indicated in references 32 and 33. The partially converted film was further condensed by continued heating in an air oven for 3 hours at  $325^\circ\text{ C}$  ( $598^\circ\text{ K}$ ). After this latter treatment, the film appeared to be black by reflected light but deep red by transmitted light. In the latter stages of conversion these films exhibit very high extinction coefficients in the visible and in the infrared portions of the spectrum. In general, the films produced by these techniques have been clear, tough, and flexible. Some properties are given in table III.

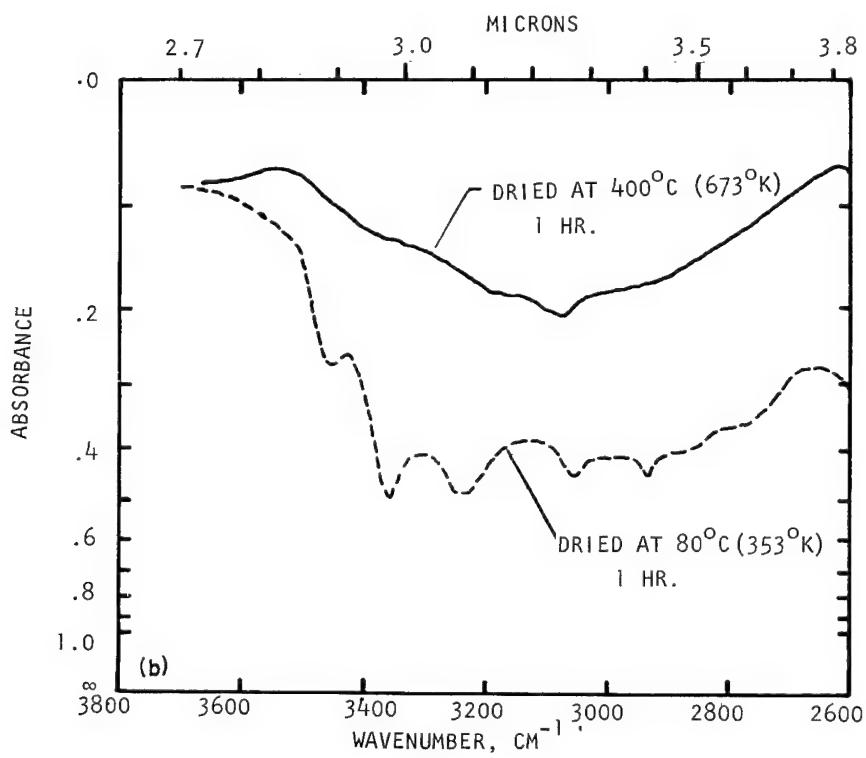
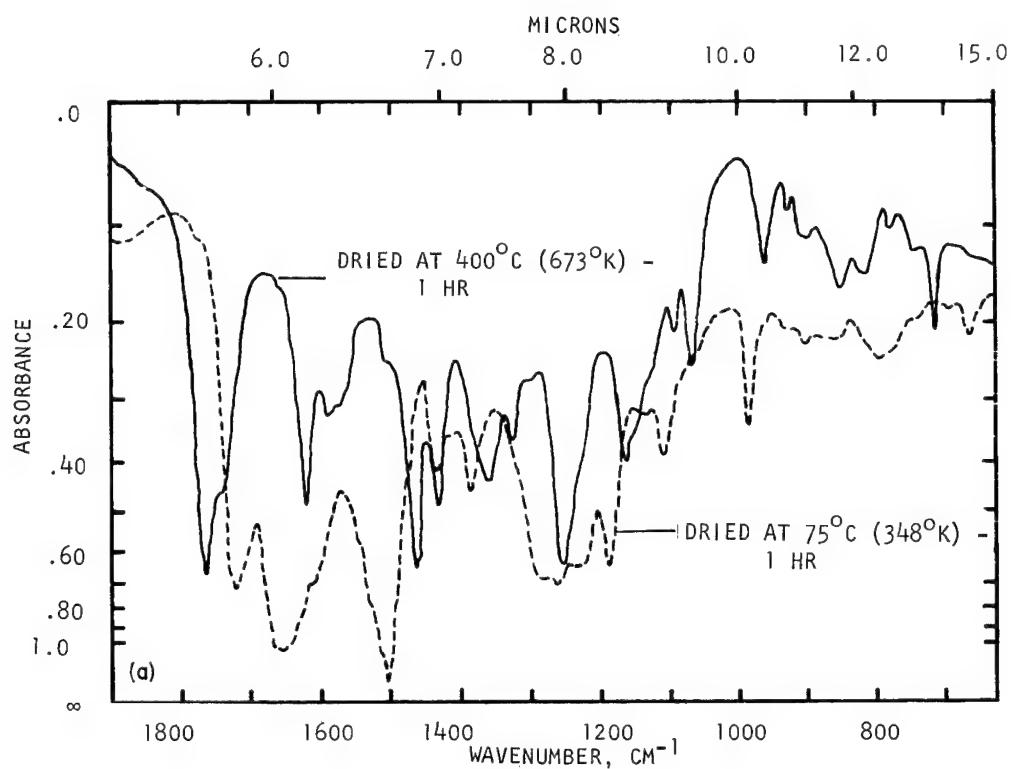


Figure 5.- Infrared spectra of 0.15-mil-thick ( $3.81 \times 10^{-4}$  cm) PMDA-TADPO polymer films.

TABLE III

## FILM PROPERTIES

	A-A-A Polymers	Pyrrones
Tensile strength . . . . .	$\begin{cases} 10\ 000 \text{ to } 15\ 000 \text{ psi} \\ 6.9 \times 10^7 \text{ to } 10.3 \times 10^7 \text{ N/m}^2 \end{cases}$	$\begin{cases} 15\ 000 \text{ to } 22\ 000 \text{ psi} \\ 10.3 \times 10^7 \text{ to } 15.2 \times 10^7 \text{ N/m}^2 \end{cases}$
Elongation . . . . .	25 to 35 percent	3 to 7 percent
Young's modulus . . . . .	$\begin{cases} 200\ 000 \text{ to } 400\ 000 \text{ psi} \\ 137.9 \times 10^7 \text{ to } 275.8 \times 10^7 \text{ N/m}^2 \end{cases}$	$\begin{cases} 600\ 000 \text{ to } 1\ 000\ 000 \text{ psi} \\ 413.7 \times 10^7 \text{ to } 689.5 \times 10^7 \text{ N/m}^2 \end{cases}$
Radiation resistance . . . . .	Strength unchanged at $10^{10}$ rads	Strength unchanged at $10^{10}$ rads
Specific resistivity (25° C) . . .	$6 \times 10^9 \text{ ohm-cm}$	$3 \times 10^{12} \text{ to } 5 \times 10^{12} \text{ ohm-cm}$
Field strength . . . . .	$2 \times 10^5 \text{ V/cm}$	$6 \times 10^5 \text{ V/cm}$
Color . . . . .	Yellow to amber	Orange to deep blood red

Abbreviations: N - newton; V - volt.

## Molding

Molding resin was prepared by precipitating the A-A-A polymer from solution with acetone. The precipitated resin was then washed with acetone and dried at room temperature under vacuum (1 torr). The dry powder could be molded at room temperature at pressures on the order of 25 000 psi ( $17.3 \times 10^7 \text{ N/m}^2$ ). The compressive strength of the unfilled molding was 12 000 psi ( $8.3 \times 10^7 \text{ N/m}^2$ ) and the compressive modulus was 400 000 psi ( $27.6 \times 10^7 \text{ N/m}^2$ ).

## Laminates

A few exploratory tests were made to determine if the polyimidazopyrrolones have potential as high-temperature laminating resins. A 12-percent solution of the A-A-A polymer was used to coat multiple layers of glass fabric. Although early tests of the flexural properties should not be taken as representative of optimum strength, they do indicate that the flexural and compressive properties were little affected at elevated temperatures as shown in table IV.

TABLE IV

## FLEXURAL AND COMPRESSIVE PROPERTIES OF PMDA-DAB

Test temperature	Flexural				Compression			
	Strength		Modulus		Strength		Modulus	
°F	°K	psi	N/m <sup>2</sup>	psi	N/m <sup>2</sup>	psi	N/m <sup>2</sup>	
Room temp.	Room temp.	12 700	$8.76 \times 10^7$	$0.70 \times 10^6$	$483 \times 10^7$	9 600	$6.62 \times 10^7$	$2.45 \times 10^6$
*600	588	7 800	5.38	.88	607	10 400	7.17	3.21
*700	644	10 100	6.96	.82	565	6 600	4.55	2.67
								1841

\*Test included 1/2-hour preheating in air at test temperature.

### Solution Properties

The intrinsic viscosity in DMF at 25° C (298° K) and the number average molecular weight ( $\bar{M}_n$ ) given in table V are typical of condensation polymers. The number average molecular weight was determined at 37° C (310° K) by using a 450 gel cellophane membrane in an automatic osmometer.

TABLE V

### SOLUTION PROPERTIES

	A-A-A polymers	Pyrrones
Intrinsic viscosity (DMF) . . .	0.6 to 1.5 deciliters/g	Insoluble
$\bar{M}_n$ (osmotic pressure) . . . . .	7000 to 22 000	Insoluble
Solvents . . . . .	DMF, DMAC, DMSO, NMP, and PPA	Insoluble

### Thermophysical Properties

The fused aromatic and heterocyclic ring structure of the polyimidazopyrrolones would be expected to provide extensive electron delocalization and hence result in exceptional thermal and radiolytic stability. As previously mentioned, pyrolytic graphite which has a high degree of delocalization has frequently been considered to be near the extreme case of a thermally stable polymer. From preliminary data, it is believed that the polyimidazopyrrolones are tractable precursors to pyrolytic graphite. Figure 6 shows the comparative thermogravimetric analysis (TGA) of a polyimidazopyrrolone (PMDA-DAB) and pyrolytic graphite, run in air with a heating rate of 6.66° C per minute. The weight loss of the PMDA-DAB below 400° C (673° K) is probably due to loss of some complexed solvent and some water of condensation. It is interesting to note that the maximum rates of weight loss for both materials are nearly identical.

The effect of complexed solvent and residual water of condensation on the thermogravimetric behavior of the polyimidazopyrrolones is shown in figure 7. Conversion of PMDA-TADPO from an intermediate stage of condensation (film 1) to a highly converted stage (film 2) essentially eliminates the weight loss below 500° C (773° K). The chemically related polyimide (PI) film is shown for comparison.

The exceptional thermal stability of the polyimidazopyrrolones is also apparent in their elemental analysis. The percent carbon is determined by oxidation at elevated temperatures and the values are as much as 7 percent lower than theoretical values. The identical analytical procedure gives carbon values 5 percent below theory for pyrolytic graphite. These results indicate the inadequacy of the analytical method to degrade thermally stable polymers. However, nitrogen values are in good agreement with theoretical values which may

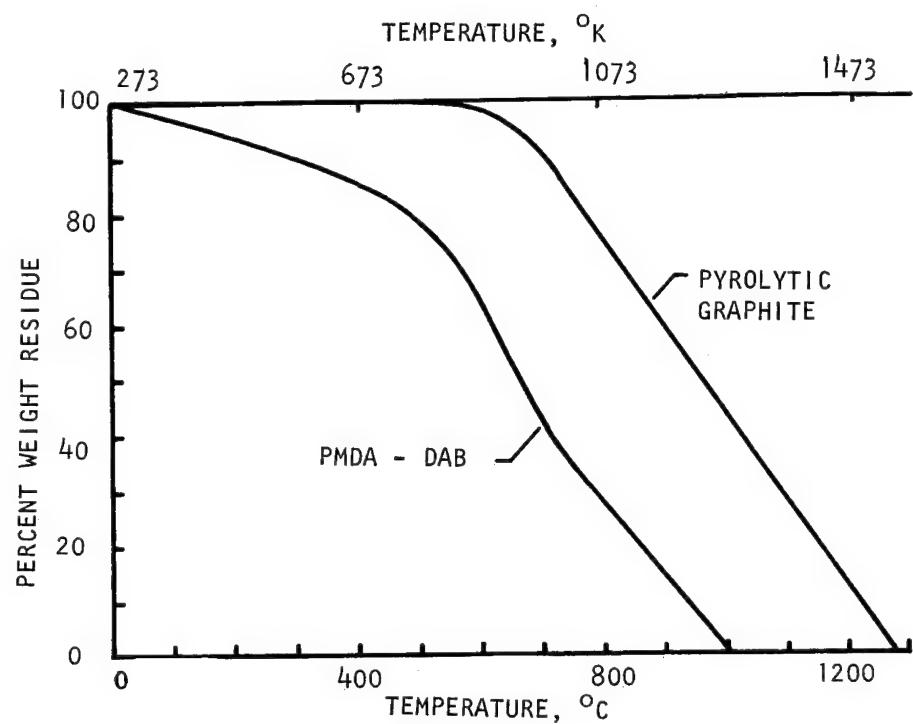


Figure 6.- Comparative thermogravimetric analyses in air.

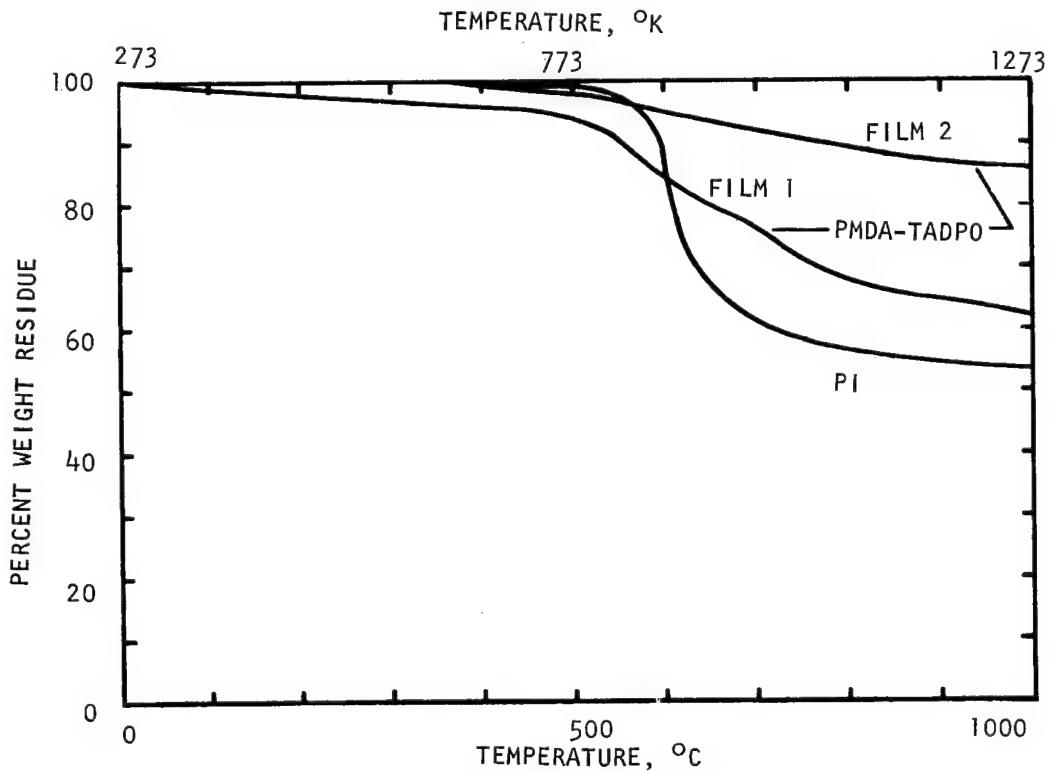


Figure 7.- Thermogravimetric analyses of a Pyrrone and polyimide in vacuum.

be accounted for by the fact that the Kjeldahl nitrogen analysis is a chemical analysis, independent of thermal stability of the material.

### Electrical Properties

The measurement of the electrical properties of the Pyrrones is aided by the fact that they have unusually good ohmic contact with vapor-deposited electrodes, which is unusual when compared with the behavior of other organic insulators with comparable high resistivity. The activation energy of electrical conduction appears to vary as a simple linear function of temperature; that is, the conduction is essentially a simple electronic process and not a complex ionic-electronic process as is the case for many organic dielectrics. This is somewhat reminiscent of the conductive processes of graphite. In the few tests run on the orange (intermediate condensation) film and the black (advanced condensation) film the activation energy for dark conductivity was 0.68 and 0.16 eV, respectively. Under proper conditions both the stepladder and the ladder polymers can undoubtedly exist as semi-conducting polymers, in that they can be made to resemble graphite closely in molecular structure and behavior. More work is required to explore the unusual electrical behavior of the poly-imidazopyrrolones and to determine their potential as semi-conducting polymers.

Power factor loss as a function of temperature has often been used as a means of determining the glass transition temperature of a polymer. Figure 8 shows the results of power-factor-loss measurements as a function of temperature on a single film during two thermal cycles up to 500° C (773° K). In the first cycle the two small peaks at 105° C (378° K) and 330° C (603° K) may be attributed to loss of water of cyclization and loss of the complexed or entrained solvent, respectively. Following the first thermal cycle, the film was cooled and a second cycle was repeated.

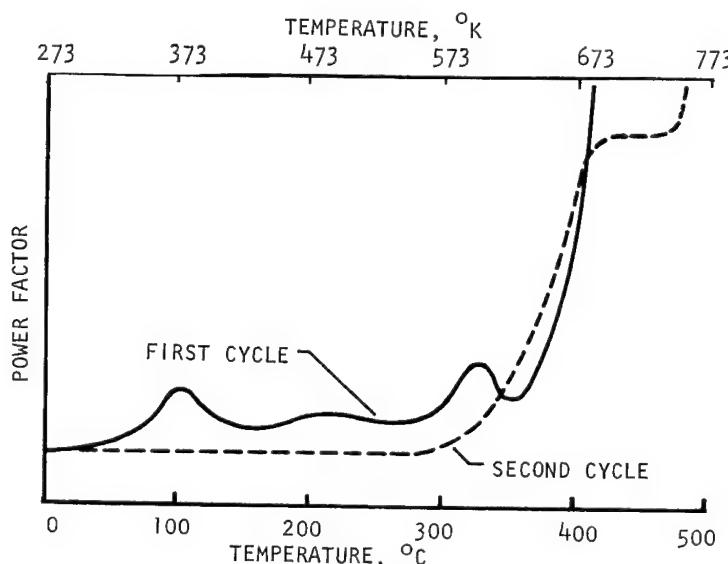


Figure 8.- Power factor as a function of temperature.

The apparent glass transition temperature of  $475^{\circ}\text{C}$  ( $748^{\circ}\text{K}$ ) is unusually high and work is in progress to study the phenomenon.

### Mechanical Properties and Radiation Stability

As anticipated, the tensile strength and Young's modulus increase with further conversion of the A-A-A polymer to the condensed Pyrrone. Condensed ring systems are generally considered to provide molecular chain stiffness and usually result in a decrease in elongation on conversion to the stepladder and ladder polymers. The radiation stability of these materials is exceedingly high (table VI), as is generally anticipated. As discussed previously, molecular chain redundancy (ladder structures) coupled with a high degree of electronic orbital overlap provides for extensive delocalization of thermal and radiolytic energies. All specimens were degassed 72 hours at  $10^{-7}$  torr and  $50^{\circ}\text{C}$  ( $323^{\circ}\text{K}$ ); the specimens were sealed at  $10^{-7}$  torr. Irradiations were carried out with a 3-MeV Dynamitron by using electron energies in excess of 2 MeV. On the basis of preliminary results, the polyimidazopyrrolones appear to be one of the most radiation-resistant polymers to be developed to date.

TABLE VI

#### EFFECTS OF HIGH-ENERGY ELECTRONS ON PMDA-TADPO

Dose*, megarad	Strength				Tangent modulus		Elongation, percent	
	Yield		Tensile		psi	$\text{N}/\text{m}^2$		
	psi	$\text{N}/\text{m}^2$	psi	$\text{N}/\text{m}^2$				
Control	9 200	$6.34 \times 10^7$	17 900	$12.34 \times 10^7$	$7.3 \times 10^5$	$503 \times 10^7$	9	
1 000	12 200	8.41	16 800	11.58	8.3	572	3	
5 000	14 300	9.86	20 200	13.93	8.2	565	3	
10 000	15 600	10.76	17 300	11.93	8.5	586	3	

\*The dose rate was 1000 megarads/hr.

### CONCLUDING REMARKS

A new class of aromatic-heterocyclic polymers has been developed. They can be easily prepared by the room-temperature reaction of aromatic tetraamines with aromatic dianhydrides in polar solvents such as dimethyl formamide. The soluble intermediate (amino-acid-amide polymer) is supported by infrared absorption spectra and correlation to the chemistry of related dye compounds. The soluble polymeric intermediate greatly enhances the potential utility of these materials through conventional fabrication techniques. Detailed curing cycles need to be developed before these materials can be used in specific applications.

---

The electrical properties can be changed as a function of conversion state and should be studied further to determine if these materials have useful semi-conductive or photoconductive properties. The polyimidazopyrrolones have excellent thermal stability and should be explored for applications which require high-temperature service. The radiation stability of these materials exceeds that of any known synthetic polymers and should be further studied for applications which require these properties.

Langley Research Center,  
National Aeronautics and Space Administration,  
Langley Station, Hampton, Va., October 1, 1965.

## REFERENCES

1. (a) Edwards, Walter M.; and Robinson, Ivan Maxwell: Polyimides of Pyromellitic Acid. U.S. Pat. Office No. 2,710,853, June 14, 1955.  
(b) Sroog, C. E.; Endrey, A. L.; Abramo, S. V.; Berr, C. E.; Edwards, W. M.; and Olivier, K. L.: Aromatic Polypyromellitimides From Aromatic Polyamic Acids. *J. Polymer Sci.*, pt. A, vol. 3, no. 4, Apr. 1965, pp. 1373-1390.  
(c) Bower, G. M.; and Frost, L. W.: Aromatic Polyimides. *J. Polymer Sci.*, pt. A, vol. 1, no. 10, Oct. 1963, pp. 3135-3150.
2. Vogel, Herward; and Marvel, C. S.: Polybenzimidazoles, New Thermally Stable Polymers. *J. Polymer Sci.*, vol. 50, 1961, pp. 511-539.
3. Brumfield, P. E.; DiGiulio, A. V.; Lebovits, A.; and Hergenrother, P. M.: Synthesis of Polythiazoles and Polyfluoroolefins. Conference on High Temperature Polymer and Fluid Research. Robert McHenry, compiler, ASD-TDR-62-372, U.S. Air Force, Aug. 1962, pp. 61-76.
4. Hergenrother, Paul M.; Wrasing, Wolfgang; and Levine, Harold H.: Polybenzothiazoles - I. Synthesis and Preliminary Stability Evaluation. *Am. Chem. Soc. Polymer Preprints*, vol. 5, no. 1, Apr. 1964, pp. 153-159.
5. Kubota, Takashi; and Nakanishi, Ryoji: Preparation of Fully Aromatic Polybenzoxazoles. *J. Polymer Sci.*, pt. B, vol. 2, no. 6, June 1964, pp. 655-659.
6. Stille, J. K.; and Williamson, J. R.: Polyquinoxalines. *J. Polymer Sci.*, pt. A, vol. 2, no. 9, Sept. 1964, pp. 3867-3875.
7. deGaudemaris, Gabriel; Sillion, Bernard; and Preve, Jaques: Heat-Stable Polymers - I. Polyquinoxalines. *Bull. Soc. Chim. France*, vol. 8, 1964, pp. 1793-1800.
8. Marvel, C. S.; and Hartzell, Gordon E.: Preparation and Aromatization of Poly-1,3-Cyclohexadiene. *J. Am. Chem. Soc.*, vol. 81, no. 2, Jan. 1959, pp. 448-452.
9. Kovacic, Peter; and Kyriakis, Alexander: Polymerization of Benzene to p-Polyphenyl by Aluminum Chloride-Cupric Chloride. *J. Am. Chem. Soc.*, vol. 85, no. 4, Feb. 1963, pp. 454-458.
10. Lilyquist, M. R.; and Holsten, J. R.: The Synthesis and Evaluation of Poly(phenylene) Triazoles as Thermally Stable Materials. *Am. Chem. Soc. Polymer Preprints*, vol. 4, no. 2, Sept. 1963, pp. 6-14.

11. (a) Korshak, V. V.; Krongauz, E. S.; Berlin, A. M.; and Gribkova, P. N.: Synthesis of Polypyrazoles. Rept. Acad. Sci. (USSR), vol. 149, no. 3, Mar. 21, 1963, pp. 602-605.
- (b) Schaefer, John P.; and Bertram, James L.: Thermally Stable Polymers - I. Polyphenylpyrazoles. J. Polymer Sci., pt. B, vol. 3, no. 2, Feb. 1965, pp. 95-98.
12. Abshire, Claude J.; and Marvel, C. S.: Some Oxadiazole and Triazole Polymers. Makromol. Chem., Bd. XLIV-XLVI, Mar. 1961, pp. 388-397.
13. Frazer, A. H.; Sweeny, W.; and Wallenberger, F. T.: Poly(1,3,4-Oxadiazoles): A New Class of Polymers by Cyclodehydration of Polyhydrazides. J. Polymer Sci., pt. A, vol. 2, no. 3, Mar. 1964, pp. 1157-1169.
14. Charlesby, A.: Atomic Radiation and Polymers. Pergamon Press (New York), 1960.
15. Pezdirtz, George F.: Nonmetallic Materials for Spacecraft. Proceedings of the NASA-University Conference on the Science and Technology of Space Exploration, Vol. 2, NASA SP-11, 1962, pp. 451-460. (Also available as NASA SP-27.)
16. Pezdirtz, G. F.: Polymers for Spacecraft. Modern Plastics, vol. 40, no. 12, Aug. 1963, pp. 123-128, 132-134.
17. Kelble, J. M.; and Bernados, J. E.: High Temperature Nonmetallic Materials. Aerospace Eng., vol. 22, no. 1, Jan. 1963, pp. 56-75.
18. Marvel, C. S.: Polyaromatic Heterocycles. Am. Chem. Soc. Polymer Preprints, vol. 5, no. 1, Apr. 1964, pp. 167-177.
19. Natta, Giulio; Pino, Piero; Corradini, Paolo; Danusso, Ferdinando; Mantica, Enrico; Mazzanti, Giorgio; and Moraglio, Giovanni: Crystalline High Polymers of  $\alpha$ -Olefins. J. Am. Chem. Soc., vol. 77, 1955, pp. 1708-1710.
20. Gorham, William F.: A New, General Synthetic Method for the Preparation of Linear Poly-p-Xylylenes. Am. Chem. Soc. Polymer Preprints, vol. 6, no. 1, Apr. 1965, pp. 73-83.
21. Burg, Anton B.: Macromolecules of Main-Group Elements (Not Containing C-C, C-O, or C-N Skeletons, or Heavy Metals). Unsolved Problems in Polymer Science, Frank R. Mayo, ed., ASD Tech. Rept. 62-283, U.S. Air Force, Mar. 1962, pp. 40-44. (Available from ASTIA as 282067.)
22. Tessler, Martin M.: Theoretical Studies on the Thermal Degradation of Ladder Polymers. ML TDR 64-151, U.S. Air Force, July 1964.
23. Brown, John F., Jr.; Vogt, Lester H., Jr.; Katchman, Arthur; Eustance, John W.; Kiser, Kenneth M.; and Krantz, Karl W.: Double Chain Polymers of Phenylsilsesquioxane. J. Am. Chem. Soc. (Commun. to Ed.), vol. 82, no. 23, Dec. 1960, pp. 6194-6195.

24. Brown, John F., Jr.: Double Chain Polymers and Nonrandom Crosslinking. *J. Polymer Sci.*, pt. C, no. 1, 1963, pp. 83-97.
25. Burlant, W. J.; and Parsons, J. L.: Pyrolysis of Polyacrylonitrile. *J. Polymer Sci.*, vol. 22, 1956, pp. 249-256.
26. Bailey, William J.; Economy, James; and Hermes, Mathew E.: Polymers - IV. Polymeric Diels-Alder Reactions. *J. Org. Chem.*, vol. 27, 1962, pp. 3295-3299.
27. Angelo, R. J.: A Linear, Fused Cyclohexane Polymer: Cyclized Poly- $\beta$ , $\beta$ -Isoprene. *Am. Chem. Soc. Polymer Preprints*, vol. 4, no. 1, Apr. 1963, pp. 32-42.
28. Anon.: Aromatic Polymers Resist Space Environment. *Chem. Eng. News*, vol. 43, no. 20, May 17, 1965, pp. 38-39.
29. Bell, Vernon L.; and Pezdirtz, George F.: Pyrrone - A New Class of Aromatic Step-Ladder and Ladder Polymers. Paper presented at the 8th National Symposium of the Society Aero-Space Materials Process Engineers (San Francisco, Calif.), May 23-26, 1965.
30. Bell, Vernon L.; and Pezdirtz, George F.: Polyimidazopyrrolones: A New Route to Ladder Polymers. To be published in the *J. Polymer Sci.*
31. Dawans, F.; and Marvel, C. S.: Polymers From ortho Aromatic Tetraamines and Aromatic Dianhydrides. To be published in the *J. Polymer Sci.*
32. Chakravarti, Gopal Chandra: Color of Complex Diazoles. *Quart. J. Indian Chem. Soc.*, vol. 1, 1925, pp. 329-338; vol. 1, 1924, pp. 19-26. (Also in *Chem. Abstr.*, vol. 19, no. 5, Mar. 10, 1925, p. 830, vol. 19, no. 16, Aug. 20, 1925, pp. 2493-2494.)
33. Porai-Koshits, B. A.; and Antoshul'skaya, M. M.: Reaction Between Aromatic Diamines and Dicarboxylic Acids - I. The Reaction of o-Phenylenediamine With Phthalic Anhydride. *J. Gen. Chem. USSR*, vol. 13, 1943, pp. 339-352.
34. Patterson, Austin M.; Capell, Leonard T.; and Walker, Donald F.: The Ring Index. Second ed., Am. Chem. Soc., c.1960, p. 1077.

*"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."*

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

## NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

**TECHNICAL REPORTS:** Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

**TECHNICAL NOTES:** Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

**TECHNICAL MEMORANDUMS:** Information receiving limited distribution because of preliminary data, security classification, or other reasons.

**CONTRACTOR REPORTS:** Technical information generated in connection with a NASA contract or grant and released under NASA auspices.

**TECHNICAL TRANSLATIONS:** Information published in a foreign language considered to merit NASA distribution in English.

**TECHNICAL REPRINTS:** Information derived from NASA activities and initially published in the form of journal articles.

**SPECIAL PUBLICATIONS:** Information derived from or of value to NASA activities but not necessarily reporting the results of individual NASA-programmed scientific efforts. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

*Details on the availability of these publications may be obtained from:*

SCIENTIFIC AND TECHNICAL INFORMATION DIVISION

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546